

USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

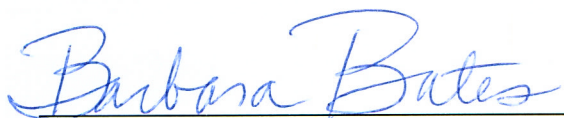
STANDARD OPERATING PROCEDURE 1251

PRECIOUS METALS ANALYSIS OF CATALYST WASHCOAT
USING A NITON XL3t FIELD-PORTABLE X-RAY
FLUORESCENCE (FPXRF) ANALYZER

Revision 1

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1 SCOPE AND APPLICATION

This standard operating procedure provides procedures for the extraction of a catalyst washcoat from small engine exhaust systems and the quantification of the precious metal content of the washcoat using X-Ray Fluorescence. Typical precious metal catalysts used in small engines are platinum (Pt), palladium (Pd), and rhodium (Rh). For small engines, the precious metals are mixed with a binding agent such as aluminum oxide and then applied as a washcoat to a ferrous metal substrate.

This SOP provides the step-by-step instructions to extract the catalyst washcoat from honeycomb-style catalyst systems; and to conduct a precious metals content analysis of honeycomb-style catalyst washcoat and substrate powders.

This SOP covers extraction of the catalyst washcoat from the catalyst substrate, and specific *NITON XL3t* X-Ray Fluorescence (XRF) precious metal content analysis procedures.

2 METHOD SUMMARY

XRF is a nondestructive qualitative and quantitative analytical technique used to determine the chemical composition of a sample. The sample is exposed to a 50kV tube x-ray source and absorbs the incident radiation. The incident radiation causes electrons to be ejected from the atomic shells of any elements present in the sample and as a result energy is released (fluoresced). The fluorescent energy is detected by the XRF analyzer as a characteristic x-ray spectrum. The x-ray spectra emitted is characteristic for each element and is the qualitative analysis. The number of counts at a characteristic energy level per unit time is representative of the element concentration in a sample and is the basis for the quantitative analysis.

The hand held, battery operated field portable *NITON XL3t* XRF analyzer is factory calibrated. Certified standards are used as the continuing calibration standards to check the initial factory calibration. The instrument performs in-situ analysis, on-site analysis of discrete samples, or laboratory analysis of prepared samples. All quality control checks must be met before XRF analysis proceeds. Data is provided verbally on-site, as a preliminary data table, and/or as a final spreadsheet.

3 DEFINITIONS

A list of terms and definitions specific to this procedure appears below. For terms and acronyms in general use at the EPA Region 9 Laboratory refer to Appendix A of the Laboratory Quality Assurance Plan.

Catalyst – Exhaust treatment device consisting of a substrate (usually metal or ceramic) coated with washcoat containing precious metals. The coated substrate is encased in a metal casing attached to engine exhaust piping inside a muffler. This entire device is a catalytic

converter, but for purposes of this SOP, the word catalyst will be used and will represent the washcoat, substrate, casing, and exhaust piping as presented in Figure 3-1. Cross Section of Catalyst Exhaust Treatment Device.

Casing – Metal sleeve encapsulating catalyst substrate material. See Figure 3-1. The casing is represented by a bold black line in Figure 3-1.

Casing inset – Difference in the length of the catalyst casing and the substrate. Often, the catalyst casing is longer than the substrate material within the casing sleeve. See Figure 3-1.

Exhaust piping – Exhaust intake piping attached to the catalyst casing. See Figure 3-1. Cross Section of Catalyst Exhaust Treatment Device. The exhaust piping is represented by a green line in Figure 3-1.

National Institute of Standards and Technology (NIST) - An agency in the United States Department of Commerce that makes measurements and sets standards as needed by industry or government programs.

Percent Difference (%D) – The difference between two values divided by the average of the two values, shown as a percentage.

Percent Relative Standard Deviation (%RSD) - The ratio of the standard error to the value being estimated, usually expressed in terms of a percentage.

Precious metals – These metals are the catalysts for the chemical reactions within the converter and are platinum (Pt), palladium (Pd), and rhodium (Rh). The metals are also referred to as platinum group metals (PGMs).

Standard Reference Material (SRM) – The SRM is a standard containing platinum group metals at known concentrations used for quality control in the XRF analysis of catalyst washcoat and substrate. SRMs are produced from recycled catalysts.

Substrate – Underlying material supporting the washcoat within the casing. The substrate is generally a ferrous metal or ceramic configured in a honeycomb pattern within a cylinder or it is wire (metal substrate only) configured in a rectangular mesh pad pattern. See Figure 3-1.

Washcoat – Coating of a high surface area solid (commonly inorganic oxides) that is the carrier for the precious metals used in the catalytic reactions within the converter. The washcoat is applied to the substrate material. See Figure 3-1.

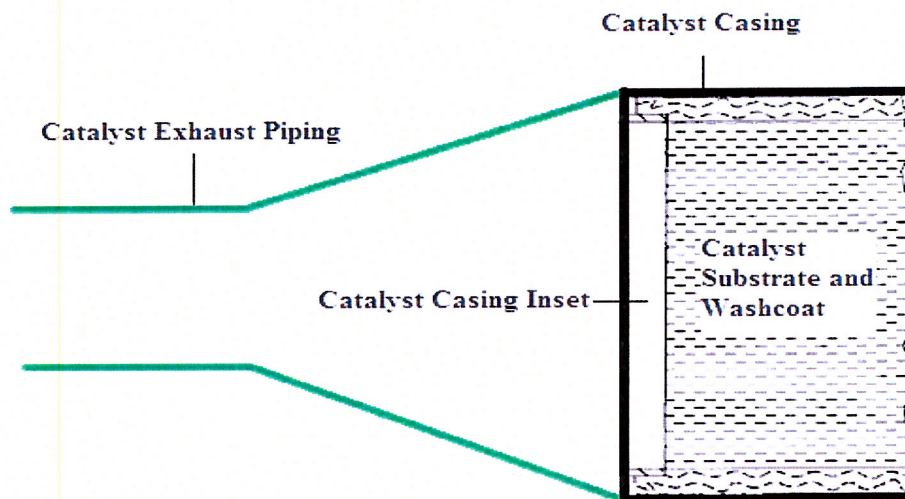


Figure 3-1. Cross Section of Catalyst Exhaust Treatment Device

4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the EPA Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections. A job hazard analysis (JHA) for this SOP has been performed and documented. The JHA is available for review on the LAN at G:\USER\SHARE\EH&S PROGRAMS\Job Hazard Analyses. The JHA identifies potential hazards associated with this work practice and provides recommended safe practices to eliminate or control hazards. All laboratory personnel must follow recommended practices identified in the JHA.”

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented room. Safety glasses and a properly fitted respirator should be worn during mechanical extraction of the catalytic converter and washcoat powder.

There are no reagents used in this procedure.

4.2 Equipment and Instruments

Follow the manufacturer’s safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

- 4.2.1 The *NITON* XL3t contains a single 50kV X-ray tube. The instrument shall only be opened by a certified *NITON* representative. If the instrument is otherwise the instrument warranty will be void.
- 4.2.2 Radiation exposure from a properly used NITON will be less than 50 millirems (mrems) per year, even if the instrument is used 2,000 hours per year. The allowable limit in the U.S. for occupational exposure is 5,000 millirems (mrem) per year for a whole-body exposure and 50,000 mrem for shallow penetration of extremities.
- 4.2.3 Exposure to radiation is related to three factors: time, distance and shielding. Refer to *NITON* User's Guide Chapter 2 for Radiation Safety.
 - 4.2.3.1 Only press the trigger to perform a measurement. Never point the *NITON* XL3t at yourself or anyone else while the trigger is depressed.
 - 4.2.3.2 Keep your hand away from the source-end of the *NITON* XL3t when the trigger is depressed. Always be aware of the instrument's radiation source and direction of beam of X-rays. The direction of the beam is clearly marked on the front and top of the *NITON* XL3t XRF.
- 4.2.4 For safe operation of the instrument, each analyst is required to complete instrument training for the *NITON* XL3t prior to operation.
- 4.2.5 Each analyst should wear appropriate personal protective equipment, including gloves and safety glasses. Hearing and respiratory protection should also be used during any cutting, grinding or milling operations.
- 4.2.6 When the XRF is not in operation, the instrument shall be stored in R9 Laboratory, Room #504.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The USEPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *USEPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

There are no reagents used in this procedure.

4.4 Waste Management

The USEPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with USEPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure*. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with USEPA Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-hazardous Waste	Not applicable
Mufflers and pipes from exhaust systems	Non-hazardous Waste for recycling	Not applicable

5 SAMPLE HANDLING & PRESERVATION

- 5.1 Samples will be collected by inspectors from the Enforcement Division. Samples are typically exhaust system parts such as pipes and/or mufflers which contain catalytic converters.
- 5.2 Shipped and delivered samples are received at the Region 9 Laboratory by staff and stored in Room 503. Sample identification and dates of collection are verified against the chain-of-custody form. Sample receiving staff will log-in the samples and assign work order and lab sample IDs. There are no special storage requirements for these samples.
- 5.3 There is not a technical holding time established for these samples.

6 INTERFERENCES

- 6.1 The total method error for XRF analysis is defined as the square root of the sum of squares of both instrument precision and user- or application-related error. Generally, instrument precision is the least significant source of error in FPXRF analysis. User- or application-related error is generally more significant and varies with each site and method used. Some sources of interference can be minimized or controlled by the instrument operator, but others cannot. Common sources of user- or application-related error are discussed below.
- 6.2 Physical matrix effects result from variations in the physical character of the sample.

These variations may include such parameters as particle size, uniformity, homogeneity, and surface condition. For example, if any analyte exists in the form of very fine particles in a coarser-grained matrix, the analyte's concentration measured by the XRF will vary depending on how fine particles are distributed within the coarser-grained matrix. If the fine particles "settle" to the bottom of the sample cup, the analyte concentration measurement will be higher than if the fine particles are mixed in well and stay mixed among the coarser-grained particles in the sample cup.

- 6.3 Inconsistent positioning of samples in front of the probe window is a potential source of error because the x-ray signal decreases as the distance from the radioactive source increases. This error is minimized by maintaining the same distance between the window and each sample. For the best results, the window of the probe should be in direct contact with the sample, which means that the sample should be flat and smooth to provide a good contact surface.
- 6.4 Ambient temperature changes can affect the gain of the amplifiers producing instrument drift. Gain or drift is primarily a function of the electronics (amplifier or preamplifier) and not the detector as most instrument detectors are cooled to a constant temperature. It is suggested that a gain check (shutter calibration) be performed if the temperature fluctuates more than 20°F.

7 APPARATUS & MATERIALS

- 7.1. Instruments and Equipment
- XRF Spectrophotometer: NITON Model XL3t
 - XRF test stand
 - Battery Charger
 - Extra batteries
 - XRF sample cups - Polyethylene sample cups: 31 millimeters (mm) to 40 mm in diameter with collar, or equivalent
 - X-ray window film: Mylar, Kapton, Spectrolene, polypropylene, or equivalent; 2.5 to 6.0 micrometers thick.
 - Polyester fiber stuffing
 - Kim Wipes
 - Permanent ink markers

For catalyst washcoat powder extraction:

- Power angle-grinder and cutting wheels;
- Reciprocating saw and blades;
- Power drill and bits;
- Extension cord;
- Work table and vise;

- Digital Scale (Precision to at least 0.01 g or less);
- Spatulas;
- Small brushes;
- Scraping tools;
- Prying tools;
- Laboratory weigh boats;
- 20-30mL glass vials;
- Wax paper;
- Scotch tape;
- Magnet (N42, Nickel Plated or equivalent);
- Safety glasses, goggles, or face shield;
- Gloves;
- Dust masks or respirator;
- Clamps;
- Small ruler; and
- Flashlight.

7.2 Reagents and Standards

Record standards and standards preparations in LIMS if relevant. In addition, if the chemical inventory bar code is missing, notify the LaSHEM (or designee) so that s/he will add the chemical to the chemical inventory database.

- 7.2.1 Blank Samples: The blank samples should be from a silicon dioxide or aluminum oxide matrix that is free of any analytes at concentrations above the method detection limits. These samples are used to monitor for cross-contamination and laboratory-induced contaminants or interferences.
- 7.2.2 Standard Reference Materials: Standard reference materials (SRM) are standards containing certified amounts of metals in catalyst washcoat matrix. These standards are used for accuracy and performance checks of XRF analyses. SRMs currently available for analysis of PGMs in catalytic converter washcoat can be obtained from the National Institute of Standards and Technology (NIST) and from (BAM), a provider of European Reference Materials (ERM) standards. NIST SRMs for this analysis include NIST 2556 and NIST 2557. The ERM standard is EB504. These SRMs contain washcoat from used automobile catalytic converters that has been analyzed using independent inorganic analytical methods by many different laboratories.

8 ANALYTICAL PROCEDURES

8.1 Instrument Setup and Calibration

- 8.1.1 Turn XRF instrument on, log in and wait for the main menu to be shown.

- 8.1.2 Let the instrument warm up for 15 minutes.
- 8.1.3 Perform an internal calibration check. Select **System Check** icon from the opening menu.
- 8.1.4 To set up the system select **Sample Type** icon. On the following screen select the **Soils & Minerals** icon. Select the **Mining Cu/Zn** icon. A Ready to Test screen appears. If you push the **Tools** icon three new choices will appear. Select the **Element Range** button. Set the ranges to 60 seconds for the main and high filters.
- 8.1.5 Filters and analysis times may also be set by clicking on the **Advanced** icon from the main menu.
 - 8.1.5.1 To set the filters and analysis times, press the **Element Range** button.
 - 8.1.5.2 On the menu that appears, set which filters will be used, and how long the analysis time for each filter will run.
 - 8.1.5.3 Return to the previous page or from the Main Menu select **Advanced**. Select **Element Sorting**. Select **Mining Cu/Zn Mode**. On this menu, select the order of the elements to be displayed and whether they will Always, Normal or Never be displayed. Save your selection.
- 8.1.6 Instrument Blank Test- A blank sample should be measured for all filters used. Select the **Analyze** button. Select the **Data** Entry button. Tap on the keyboard icon and type in the ID of the sample to be measured. Place the SiO₂ or aluminum oxide Al₂O₃ sample in front of the window, or if the analyzer is in the test stand press the **Start** button on the top left of the screen, to run an analysis. Measure the instrument blank for the same time period as planned for the samples. If elements are measured, check the instrument shutter window and Mylar sheet for contamination; then repeat the blank measurement. If one or two elements are still measured make notation in the log book of which elements and at what concentration level.
- 8.1.7 Calibration Verification Check - Measure the SRMs (NIST 2556, NIST 2557, and ERM EB504), which contain the analytes of interest at appropriate concentrations, to verify the accuracy of the instrument. The SRMs are measured for all filters used. Measure the SRMs for the same time period as planned for the samples. Calculate percent difference (%D) for each analyte. Calibration will be verified if %D is within 15% of the true value of the analyte. Refer to Appendix B for a list of elements and the acceptable ranges for each element within the calibration standards. Follow the procedure in 8.1.6 for running an analysis.

8.2 Catalyst Washcoat Extraction

The NITON XL3T analyzer requires a sufficient depth of target material being analyzed to provide meaningful results. For purposes of analyzing catalyst washcoat powder at least one gram should be extracted, if possible.

8.2.1 Honeycomb Catalyst Extraction

The washcoat for honeycomb catalysts adheres to the surfaces of the metal substrate and its cells. Depending on the cell density of the catalyst substrate, the cell openings can be extremely small (some as small as 0.25 mm) and difficult to access with tools. Therefore, this SOP calls for separating the washcoat magnetically after milling the substrate. If milling is not practical, manual techniques may be used to remove catalyst washcoat, however it may then only be possible to determine washcoat concentrations and ratios, but not loading. This may also occur if the substrate does not allow magnetic separation because, for example, it is made of stainless steel or ceramic.

In order to accomplish a precious metal loading analysis, the potential loss of any extracted washcoat must be minimized. When handling or transferring the catalyst between work areas, hold the catalyst in a horizontal position to minimize the loss of powder that may fall out of the cells. Avoid knocking the catalyst when it is not contained within a weigh boat.

8.2.1.1 Removal of Catalyst Casing and Substrate from Exhaust Assembly

Note: All measurements and notes taken in this section and sections 8.2.1.2 and 8.2.1.3 are recorded in the Sample Prep Batch Excel sheet that is stored in I:\Data\Room504_508\Catalytic Converters in the appropriate Batch folder.

- i. Photograph the sample and any part numbers that are visible. Store these photos in I:\Data\ROOM504_508\Catalytic Converters in the appropriate Batch folder.
- ii. Record the part numbers in the Sample Prep Excel sheet that is located in the appropriate Batch folder.
- iii. Weigh the entire sample on the top loading balance in Rm. 205, which can measure mass up to 5100g, to the 0.1-gram level. If the sample is too heavy for this balance, weigh the sample on the scale in the warehouse, Rm. 500, and convert lbs. to grams.

- iv. Using an analytical balance weigh a weigh boat to 10 mg accuracy or better. Record the weight and write it on the lip of weigh boat.
- v. Weigh several empty 15 mL (or other suitable size) glass vials on the scale. Record the weight. Write the weight on the lid of the vial.
- vi. Take the sample to Room 508.
- vii. Remove the catalyst casing and substrate from the exhaust assembly by opening the assembly with a pipe cutter, angle grinder or reciprocating saw.
- viii. Place the removed catalyst in a pre-weighed weigh boat.
- ix. Retain all left over parts and cuttings in a large re-sealable zipper storage bag.

8.2.1.2 Catalyst Measurement

- i. Cover work table area with wax paper or other suitable impervious surface to catch spills and pieces of material that may fall outside the weigh boat. Do not use fibrous paper such as writing and copying paper. Fibrous paper can provide collection points making it difficult to reclaim and preserve all of the washcoat.
- ii. Measure the diameter and length of the substrate to at least 1 mm accuracy using the digital caliper and metal ruler. Record the data in the Sample Prep Excel sheet.
 - a. The diameter is measured 4 times and averaged. Measure the thickness of the outer casing, multiply by 2 and subtract from the measurement of the catalyst (including casing).
 - b. Measure the length of the casing and if there is any free space between the casing and catalyst, subtract from the total length.
- iii. Photograph the extracted catalyst, including the honeycomb, and any part numbers that are visible. Store these photos in I:\Data\ROOM504_508\Catalytic Converters in the appropriate Batch folder.
- iv. Record the part numbers in the Sample Prep Excel sheet.
- v. Print the photograph of the honeycomb and use the photograph to count the number of cells. If all cells are not visible from the photograph, manually count the cells as noted. If counting is

performed manually, use a hand held tally counter. If the number of cells exceeds 400, use a delimiter to count a smaller area. Repeat the count in another part of the substrate. Use the average, and dimensions of the substrate face and the delimiter to calculate the total count. Record in the Prep Log file.

- vi. Using a pre-weighed weigh boat, weigh the catalyst and record the weight.

8.2.1.3 Washcoat Extraction

Mechanical extraction involves drilling/milling out the substrate and washcoat powder. Care should be taken to minimize the loss of metal and powder drifting outside of the workspace. Safety glasses and respirator should be worn while drilling.

- i. Set up the work bench, wipe clean, and secure a piece of wax paper to the work bench.
- ii. Affix the catalyst in a vise, elevated from the workbench surface and place the weigh boat under the catalyst to collect the extracted material. Place the weigh boat directly under the catalyst in a way that the drilled out material will be caught entirely into the weigh boat.
- iii. Select an end mill no smaller than 1/2 inch (12.7 mm). Affix in the drill press chuck.
- iv. Begin drilling into the catalyst substrate as perpendicular as possible to the face of the catalyst substrate. It is important to drill very slowly to finely grind the catalyst, produce clean holes, and not break the structure. Drill completely through the length of the catalyst in a position on the catalyst surface that allows adjacent holes to be drilled. Ensure that the catalyst material that is drilled falls onto the weigh boat. The end mill can only drill to a maximum depth of 2 1/2 inches (50 cm). If the catalyst is longer, drill from one end as far as possible and then flip the catalyst over and position it in the vise so that a hole drilled from the other end will meet the original hole as closely as possible.
- v. If more powder is needed, affix the catalyst back into the vice and repeat IV. Drill a second hole perpendicular to the catalyst face in a way that will not enter into the first hole.
- vi. Using a small brush, wipe the drill bit down and collect the metal and powder in the weigh boat.

- vii. Obtain one pre-weighed glass vial and label with the work order number.
- viii. Using a new glass vial, separate the metal from the powder using a magnet as described below. Continue use of the magnet until no additional metal substrate is visible.
 - a. **NOTE:** If using rare earth magnets, note they are very strong and can be difficult to work with. Always perform magnetic separations with some type of media (paper, glass, weigh boat) between the powder/metal and the magnet. The metal is extremely difficult to remove from the magnet and material losses may occur. Also, the rare earth magnets should be stored and handled away from electronic devices, especially with memory storage that can be damaged if placed near the magnet.
 - b. With the cap on a glass vial containing the washcoat powder, orient the vial so it is horizontal and slowly rotate the vial, holding the magnet on the top side of the vial. The metal in the powder will attach to the side closest to the magnet and the non-ferrous powder will drop to the bottom side of the vial.
 - c. Rotate the vial multiple times until all of the metal has been removed from the powder.
 - d. With the magnet still holding the metal to the top side of the vial, carefully remove the cap of the vial and pour the washcoat powder into the pre-weighed glass vial (see Step VII above) and re-weigh the vial. Record the weight.
 - e. Remove the magnet, and pour the metal back into the original pre-weighed weigh boat. Weigh the metal and record the weight.

8.3 Sample Preparation for XRF Analysis

The following section describes the procedures for preparing samples of powder washcoat and substrate from honeycomb catalysts to be analyzed using the NITON XL3t XRF.

8.3.1 Preparing XRF Sample Cups for Powder Washcoat Analyses

- i. Gather the tools and materials needed for analysis (Figure 8-1):

- Static-free weighing dish
 - Polyester fiber stuffing
 - Forceps
 - Whatman filter circles (2.4 cm)
 - Sample cups (25 mm)
 - Sample cup rings
 - Sample cup lids
 - Mylar film
- ii. Secure Mylar film on sample cup:
- a. Using forceps, place a sheet of Mylar film over the indented side of the sample cup (Figure 8-2). Do not touch the section of film that goes over the open surface of the cup.
 - b. Place a sample cup ring (with the ring side down) over the Mylar film and press the ring down (Figure 8-2). The ring will snap into place. Check the film for any signs of tearing. To reduce interference, ensure that the Mylar sheet is pulled tightly across the top of the sample and there are no wrinkles or bubbles in the Mylar. The outer ring slides on the cup easier if the ring is angled slightly until it starts sliding down the cup sides. Figure 8-2 shows the step-by-step procedure for sealing the sample cup.
- iii. Transfer the washcoat powder from the glass vial to a sample cup:
- a. Place the 15-mL glass vial with the washcoat powder and an empty sample cup in a weigh boat, as shown in Figure 8-2.
 - b. Transfer washcoat powder from the vial to the empty sample cup. Typically, all of the washcoat is transferred to the sample cup. The sample should contain at least 1 gram of washcoat.
 - c. Transfer any powder washcoat spilled onto the weigh boat during the cup filling process back into the glass vial.
 - d. Place a Whatman circle filter over the powder washcoat as shown in Figure 8-2.
 - e. Using a generous portion of the polyester fiber stuffing, fill the remaining free space in the sample.
 - f. Seal with the sample cup lid.
 - g. Label the side of the sample cup with the lab ID number or at least the last four digits of the catalyst VIN or serial number using a Sharpie pen.

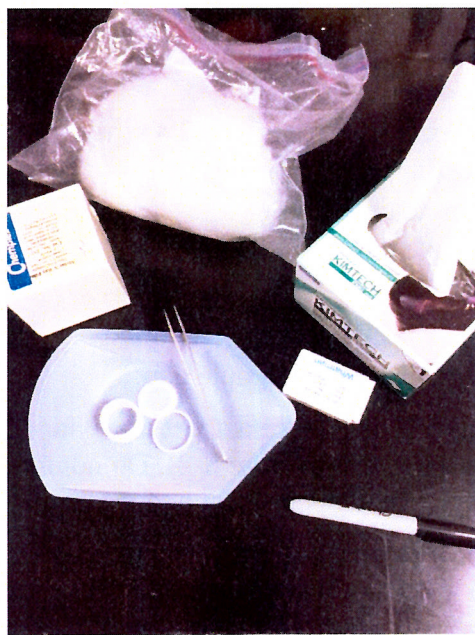


Figure 8-1. Materials needed to prepare sample cup with washcoat powder for analysis.

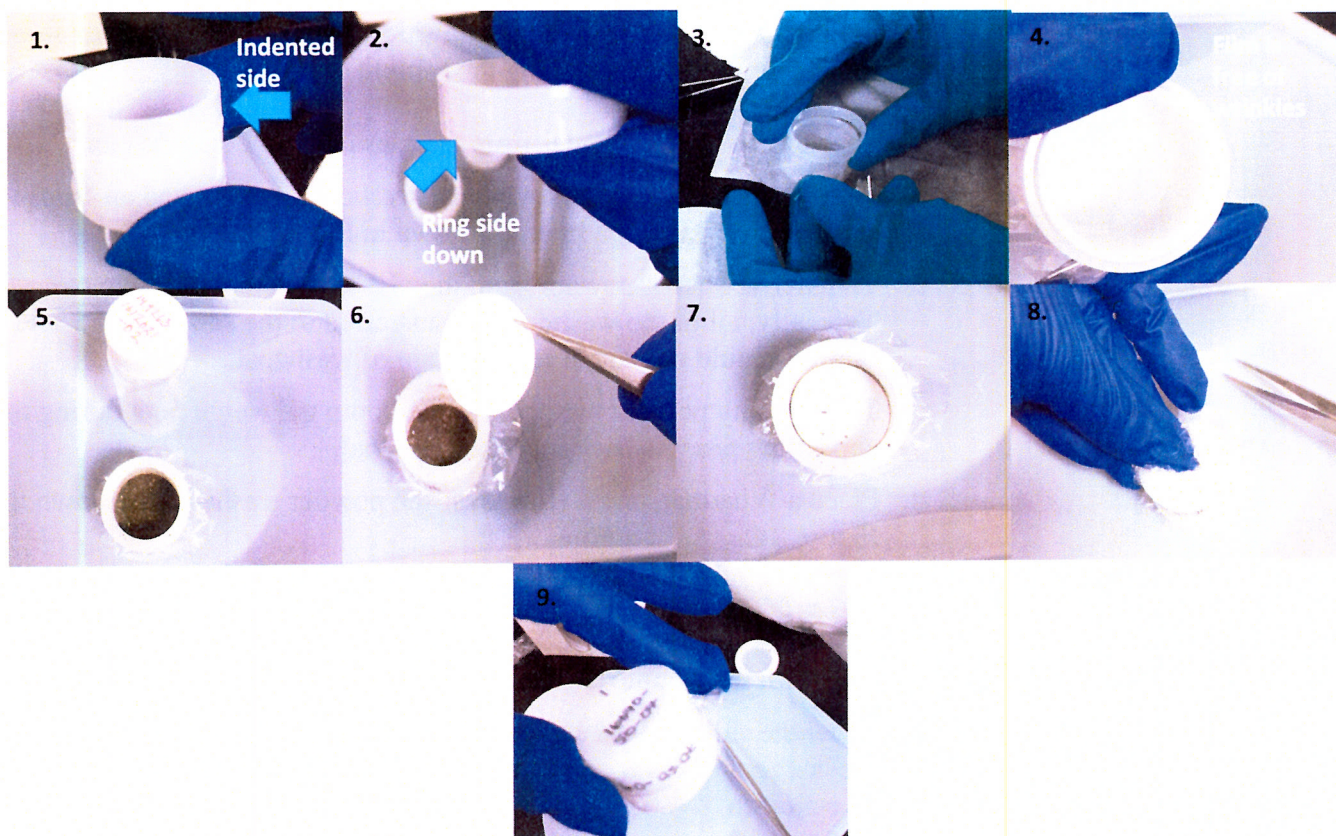


Figure 8-2. Steps for Preparing a Sample Cup with washcoat powder for XRF analysis

8.4 Analyzing Samples Using the NITON XL3t

8.4.1 Analyzing Powder Washcoat and Substrate Samples

This section describes the process for analyzing powder washcoat and substrate extracted from catalysts for precious metals content.

i. Analytical Sequence

Below is an example of a typical analytical sequence, including number of replicates.

1. System Check
2. SiO₂ Blank (1X)
3. NIST 2556 (3X)
4. NIST 2557 (3X)
5. ERB EB504 (3X)
6. Sample 1 (3X)
7. Sample 2 (3X)
8. Sample 3 (3X)
9. Sample...X (3X)
10. SiO₂ Blank (1X)
11. NIST 2556 (3X)
12. NIST 2557 (3X)
13. ERB EB504 (3X)
- (End)

- ii. Initiate sample analysis. Once all test conditions are set and the sample is in place, pull the trigger or if the analyzer is in the test stand press the “Start” button on the top left of the screen. An orange light will illuminate on the instrument and on the stand. When the analysis is complete the light will turn off. You can also stop the analysis by releasing the trigger or pressing the “Stop” button located next to the “Start” button. Repeat the analysis at least three times.

WARNING: Do not lift the lid on the unit while a test is in progress and the orange light is illuminated. The unit is emitting X-ray radiation. The programming is interlocked to shut down if the lid is lifted but the lid is not latched.

iii. View Data:

- a. Once the analysis is complete, the orange light on the handle of the XRF and/or on the stand will shut off. To view the data return to the main menu and select the **Data** icon. Select the

View Data icon from the next screen. Results for the analysis should be displayed in the table on the screen.

- b. Press the left or right arrows on the key board or below the screen on the instrument to display results of different sample runs.
- iv. Remove sample from measurement window:
 - a. Once the analysis has concluded, lift the lid and remove the sample from the measurement window. Verify that the orange light on the handle of the XRF is not illuminated prior to opening. Remove the sample and close the top.
 - b. Place the labeled sample in an empty recycled pipette tip box. Label the box with the work order or Batch #.
 - c. Follow proper evidence handling procedures to store the catalyst and powder.
- v. To export the data:
 - a. On the PC, open the NITON Data Transfer software. Select the “Download” button at the top of the main interface screen.
 - b. Press the “Query Readings” button.
 - c. Select the destination folder and file name for the exported file. Once the appropriate pathway is selected, press the “Download” button that is below the “Query Readings”
- vi. Input results into the precious metals analysis worksheet (see Attachment F).

9 QUALITY CONTROL

The EPA Region 9 Laboratory operates a formal quality control program and tracks compliance using the Lab QC Database. As it relates to this SOP, the QC program consists of a demonstration of capability, and the analysis of a standard blank and three reference standards at the beginning and end of each analysis as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated.

9.1 Demonstration of Capability

A demonstration of capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in USEPA Region 9 Laboratory SOP 880 *Demonstration of Capability*.

9.2 Instrument QC

- 9.2.1 Internal Calibration Check - In order to begin measurements, a self-calibration must be performed on the XRF. Once the user has logged on and the instrument is warmed up, the instrument will be at the main menu. Select **System Check** button from the opening menu and click **Analyze**. The instrument will then perform an internal calibration. The results will be stored in the instrument.
- 9.2.2 Calibration Verification Checks - A calibration verification sample is used to check the accuracy of the instrument and to assess the stability and consistency of results for the analytes of interest. Perform a sample control check at the beginning and end of each analysis.
- 9.2.2.1 NIST or Equivalent SRM – Use the reference standard containing the analytes of interest at appropriate concentrations to verify accuracy of instrument. Refer to Section 8.1.7.
- 9.2.2.2 Percent Difference (%D) - All standards are analyzed in triplicate. The measured value for each target analyte should be + or - 15% of the value considered accurate in order for the calibration verification check to pass. Refer to Appendix B for a list of analytes and their true values. If the %D falls outside of this acceptance range recheck the internal calibration. If the *NITON XL3t* XRF does not successfully calibrate after three attempts, contact the NITON service department at (401) 294 -1234.
- 9.2.2.3 Instrument Blank - The instrument blank should be analyzed daily before and after analyses are conducted and whenever contamination is suspected. An instrument blank verifies that no contamination exists in the spectrometer or on the probe window. Examples of instrument blanks are silicon dioxide powder or aluminum oxide powder.

9.3 Batch QC

9.3.1 Duplicates

All samples are analyzed in triplicate. Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|C_{md} - C|}{(C_{md} + C) / 2} \times 100$$

Where
RPD = relative percent difference.

C_{md} = measured concentration in the MD, corrected dilutions.
 C = measured concentration in the routine sample, corrected for dilutions.

The RPD limit for all analytes is ≤ 20 . If the RPD limits are exceeded, the cause of the exceedance must be determined and corrected and the sample must be re-analyzed.

10 DATA ACQUISITION, REDUCTION and DOCUMENTATION

10.1 Data Elements in LIMS

- 10.1.1 Standards – Record all standards in the LIMS. Store certificates of analysis associated with standards in the LIMS.
- 10.1.2 Analytical Data – Analytical data are stored in Excel sheets. Convert all Excel sheets to PDF and attach to the Batch in LIMS.
- 10.1.3 Review Forms – The analyst completes a fillable-PDF review form for each reportable analytical batch or sequence and attaches it to the proper LIMS batch or sequence. The reviewer (i.e., supervisory staff or senior analyst) completes his/her portion of the review form after reviewing and approving the associated data.

10.2 Automated Instrument Data

All data (not just reported data or acceptable runs) generated on an automated instrument are to be backed up to the LAN (I:\Data\ROOM504_508\Catalytic Converters\[Batch name]) routinely. This includes runlogs in whatever form the data system uses. Additionally, the runlog must be in a format accessible via a text editor or pdf viewer (e.g. file extensions .pdf, .csv, .txt, etc.).

The XRF instrument has software capable of storing all analytical results and spectra. The downloaded data can be exported into spreadsheet programs for further analysis and reporting. A copy of the raw data should be scanned and imported to the LIMS. Instructions on data downloading and file export are contained in Appendix C.

- 10.3 During data reduction the following information should be considered. The instrument will report concentration and the precision range in mg/Kg. The XRF will report a detection if the measurement value is at least three times the standard deviation of the measurement. The measurement precision represents a 95% (or “2-sigma”) confidence interval around the measured value. An element is classified as detected if the measured concentration is at least 1.5 times the precision.
- 10.4 The quantitation limit of the instrument should be 2 times the MDL, as established according to the Region 9 Lab SOP 880 (3.14 times the standard deviation of 7

replicate analyses conducted over 3 days, of a standard 3-5X the anticipated MDL). Site specific MDL's may be determined by performing 7 replicate analyses of site specific samples, and determining the MDL for that site specific matrix. Since XRF analysis is dependent on the sample texture and composition, decisions about the choice of QL for a project should be made based on the DQOs for the project, and site specific knowledge of the project staff.

10.5 XL3t RESULTS

Catalysts are typically certified with two separate specifications related to precious metals: precious metals ratios and precious metals loadings. The following sections describe how the measured results of the procedures in this protocol are used to calculate the ratios and loadings of precious metals, which can then be compared to the certified values for compliance determination by EPA.

10.5.1 Precious Metals Ratio Calculations

Equation 1 calculates the ratio of the three precious metals in the sample washcoat using the raw concentrations reported by the XL3t (in ppm or percent). Equation 1 assumes that Rh is the lowest concentration metal for the purpose of presenting an example. The ratios of the three precious metals should always be calculated using the lowest concentration metal as the common denominator.

Equation 1

$$Ratio = \frac{Conc_{Pt}}{Conc_{Rh}} : \frac{Conc_{Pd}}{Conc_{Rh}} : \frac{Conc_{Rh}}{Conc_{Rh}}$$

10.5.2 Precious Metals Loading Calculations

There are four equations used to calculate precious metals loadings. Equation 2 shows the relationship between total active material loading, the certified parameter, and the individual concentrations of each precious metal. Equation 3, 4, and 5 provide separate calculations necessary to use Equation 2.

Equation 4 calculates the volume of the catalyst analyzed by the XRF depending on the catalyst type. This volume represents the volume of catalyst that is drilled out of the catalyst to create the powder sample.

Equation 4 assumes that the drilled hole is perpendicular to the catalyst substrate and that the resultant drilled hole is a perfect cylinder. The accuracy of the volume calculated in

Equation 4, and consequently the loading values of Equation 2, is limited by

these assumptions. Human operation ensures that the drilled hole is not perfectly perpendicular or perfectly cylindrical. **Therefore, the loadings values calculated are considered screening-level results.**

Equation 5 calculates a Substrate Correction Factor (*SCF*), which accounts for any precious metal remaining with the ground substrate grindings after the magnetic separation process. The factor is determined by performing a separate XRF analysis for precious metals on the remaining ground substrate. The *SCF* is calculated using the mass of substrate after separation of the washcoat and the results for the precious metal (Pt, Pd or Rh) measured at the highest concentration in the substrate. Using the result for the metal present at the highest concentration ensures the most accurate measure of washcoat remaining with the metal substrate after magnetic separation.

Equation 2

$$\text{Metal Loading} = \left(\frac{W_{Pt} + W_{Pd} + W_{Rh}}{V_c * 3.53147 * 10^{-5} \text{ ft}^3} \right) * SCF$$

$$= \text{Total Active Material Loading, } \frac{\text{g}}{\text{ft}^3}$$

Equation 3

$$W_{Pt, Pd, \text{ or } Rh} = \text{Conc}_{Pt, Pd, \text{ or } Rh} / 1,000,000 * W_c$$

Equation 4 – For mechanical extraction using an end mill

$$V_c = L_c \times \frac{D^2}{4} \times \pi \times \text{number of drill holes}$$

Equation 5 – Substrate correction factor, *SCF*.

$$SCF = \frac{W_c \text{ Conc}_{Pt, Pd, \text{ or } Rh} + W_s \text{ Conc}_{Pt, Pd, \text{ or } Rh}}{W_c \text{ Conc}_{Pt, Pd, \text{ or } Rh}}$$

Where:

Conc Pt, Pd, or Rh = Concentration of metals in parts per million by weight

*W*_{Pt, Pd, or Rh} = Weight of individual metals analyzed, grams

*W*_c = Weight of washcoat analyzed, grams (for honeycomb catalysts);

*W*_s = Weight of substrate grindings remaining after washcoat separation

SCF = Substrate Correction Factor, dimensionless

D = Drill bit diameter, cm

*L*_c = Length of hole drilled through the catalyst, cm

*V*_c = Volume of catalyst, cm³

10.6 Analytical Report and Data Package

An electronic data package shall be prepared for each project. The electronic data package should include: a case narrative; results spreadsheet; raw data printouts; copies of run logs and notebooks; and any sample chain-of-custody documentation. Analytical reports are produced using the LIMS.

10.7 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance;
- Subsequent instrument modifications and upgrades, including major software upgrades;
- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with USEPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.8 SOP Distribution and Acknowledgement

After approval, distribute an electronic copy of the final SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. (The Laboratory QC Database contains a list of assigned analysts for each SOP). All approved EPA Region 9 Laboratory SOPs are maintained in the LAN in Adobe Acrobat portable document format.

Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.9 SOP Revisions

Revisions to this SOP are summarized in Appendix F.

11 REFERENCES

EPA Region 9 Laboratory documents (SOPs, the Laboratory Quality Assurance Plan, etc.) are not included in this list. Analysts are referred to the SOP database on LotusNotes or the local area network (G:\USER\SHARE\QA PROGRAM\LAB SOPS PDF) for these documents; laboratory users should contact the Chemistry Team Leader or Laboratory QAO for copies of any supporting documents.

U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response.
Method 6250, X-Ray Fluorescence Spectrometry for the Determination of Elemental

Concentrations in Environmental Matrices, Draft March 2000.

NITON XL3t Series User's Guide Version 5.2

California Department of Toxic Substances Control, Standard Operating procedure for metals Determination in Soil by NITON 702 XRF, Rev. 0, January 1999.

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd ed.; U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, 1996; SW-846.

Environmental Technology Verification Report, Field portable X-ray Fluorescence Analyzer, NITON XL Spectrum Analyzer, U.S. Environmental Protection Agency, EPA/600/R-97-150, March 1998

Standard Operating Procedure Precious Metals Analysis of Catalyst Washcoat Draft, U.S. Environmental Protection Agency Office of Enforcement and Compliance Assurance, January 3, 2014

APPENDIX A
ANALYTE LIST

<i>Analyte</i>	<i>Chemical Abstract Services Registry Number (CASRN)</i>	<i>Filter to be used for detection of analytes</i>	<i>Region 9 Laboratory Quantitation Limits (mg/Kg)</i>
<i>Palladium (Pd)</i>	<i>7440-05-3</i>	<i>High</i>	<i>40</i>
<i>Platinum (Pt)</i>	<i>7440-06-4</i>	<i>Main</i>	<i>160</i>
<i>Rhodium (Rh)</i>	<i>7440-16-6</i>	<i>High</i>	<i>40</i>

APPENDIX B
STANDARD REFERENCE MATERIALS**Standard Reference Material 2556****Used Auto Catalyst**
(Pellets)

(In Cooperation with the International Precious Metals Institute)

This Standard Reference Material (SRM) is intended for use in evaluating chemical and instrumental methods for the analysis of platinum group metals and lead. It is a recycled pellet auto catalyst in the form of fine powder (less than 74 μm (-200 mesh)). This SRM is issued in 70 g units.

Certified Values

Element	Concentration, mg/kg		Method
Pt	697.4	± 2.3	ID-TIMS
Pd	326.0	± 1.6	ID-TIMS
Rh	51.2	± 0.5	ICP-MS
Pb	6228	± 49	ID-TIMS

The certified values for platinum, palladium, rhodium and lead were determined on samples that were calcined for 2 h at 500 °C prior to analysis, and are based on results obtained using isotope dilution thermal ionization mass spectrometry (Pt, Pd, Pb) or inductively coupled plasma mass spectrometry (Rh). The stated uncertainties are 99 % confidence intervals of the single method means.

APPENDIX B (continued)**Standard Reference Material 2557****Used Auto Catalyst
(Monolith)**

(In Cooperation with the International Precious Metals Institute)

This Standard Reference Material (SRM) is intended for use in evaluating chemical and instrumental methods for the analysis of platinum group metals and lead. It is a recycled monolith auto catalyst in the form of fine powder (less than 74 μm (-200 mesh)). This SRM is issued in 70 g units.

Certified Values	
Element	Concentration, mg/kg
Pt	1131 \pm 11
Pd	233.2 \pm 1.9
Rh	135.1 \pm 1.9
Pb	13931 \pm 97

The certified values for platinum, palladium, rhodium, and lead were determined on samples that were calcined for 2 h at 500 °C prior to analysis, and are based on results obtained using isotope dilution thermal ionization spectrometry (Pt, Pd, Pb) or inductively coupled plasma mass spectrometry (Rh). The stated uncertainties are 99 % confidence intervals of the single method means.

APPENDIX B (continued)

CERTIFICATE OF ANALYSIS
ERM[®]-EB504

Platinum Group Elements in Used Automobile Catalyst			
	Certified value ¹⁾	Uncertainty ²⁾	
Element	Mass fraction in mg/kg		
Pt	1777	±	15
Pd	279	±	6
Rh	338	±	4

¹⁾ Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of measurement. The values are traceable to the SI (Système International d'Unités) by the use of sufficiently pure substances of known stoichiometry for calibration.

²⁾ Estimated expanded uncertainty *U* with a coverage factor of *k*=2, corresponding to a level of confidence of about 95 %, as defined in the Guide to the Expression of Uncertainty in Measurement (1995) ISO, Geneva.

APPENDIX C DATA DOWNLOADING AND FILE EXPORT

- 1) Start the XRF analyzer. You do not need to Log In for data transfer.
- 2) Connect the XRF analyzer to the computer via the USB/ mini USB cable.
- 3) Open the NITON Data Transfer Software (Version NDT 7.2.2).
- 4) From the Main menu select **Download**.
- 5) A query page will appear. If the analyzer is connected and communicating the Connect button will be grayed and the Disconnect button will be black. You can check the connection by pressing the **Test** button. If the unit is connected a message will appear, "Hardware successfully communicating". Press **OK**.
- 6) Identify a destination folder for the data.
- 7) Press the **Query Readings** button.
- 8) A list of files available for downloading from the instrument will appear. Select the files to be downloaded by checking each box or select "All" or "Soil" from the Reading Types box.
- 9) Press the **Download** button. When complete the unit will show 100% on the progress bar. Check the "Simultaneous Download to MS Excel" to have the data also downloaded in an excel spreadsheet format. Click **Done** when complete.
- 10) The data will then appear in an Excel file on the computer screen, as well as in the NDT software as an ndt file. The data can be edited, deleted, etc. in these programs. A complete unmodified raw data file should be kept for any analyses. Edited versions should be noted as such.
- 11) Save the Excel file as the Batch name and place in the I:/Data/Room504_508/Catalytic Converters/[Batch folder name].

**APPENDIX D
PREPARATION LOG**

Sample ID	L6FB6NAJ1F0000126	L8YSCKLB8EYC80014	L8YSDNLF8EYC80015
Engine Family			
Lab ID	1504044-01*	1504044-02*	1504044-04
Mass intact exhaust system provided (g)	2474.2	1075.9	810.4
Mass of weigh boat	7.487	7.429	7.518
Mass of cut Catalytic converter + weigh boat(g)	1261.7	253.61	166.221
Mass of cut Catalytic converter (g)	1254.213	246.181	158.703
Mass of left over converter material (g)	1253.2	245.67	157.981
Mass of washcoat (g)	1.003	0.374	0.734
Missing monolith (g)	0.01	0.137	-0.012
% Monolith missing (%)	0.00	0.06	-0.01
Cell count	1856	252	169
Monolith length (cm)	11.02	9	9.01
Monolith diameter (cm)	8.705/8.688/8.683/8.667	3.274/3.306/3.314/3.303	3.966/3.975/3.972/3.975
Monolith diameter average (cm)	8.686	3.299	3.972
Monolith volume (cm ³)	653.0	76.9	111.6
Mass empty vial (g)	15.093	15.107	15.269
Mass vial plus washcoat (g)	16.096	15.481	16.003
Mass of washcoat (g)	1.003	0.374	0.734
Mass empty vial 2 (g)			
Mass vial plus remaining ground substrate (g)			
Mass of remaining ground substrate (g)			

SOP 1251 R1.docx

[illegible]

**APPENDIX F
REVISION HISTORY****STANDARD OPERATING PROCEDURE: 1251****Revision: 1, Effective: 01/09/17****PRECIOUS METALS ANALYSIS OF CATALYST WASHCOAT
USING A NITON XL3t FIELD-PORTABLE X-RAY
FLUORESCENCE (FPXRF) ANALYZER**

Revision	Effective Date	Description
0	06/01/15	1. Initial Revision. Prepared in accordance with SOP 850 <i>Preparation of Standard Operating Procedures</i> .
1	01/27/17	1. Definition and specification of Standard Reference Materials instead of Catalyst Calibration Standards for XRF quality control. 2. Specification of mechanical washcoat extraction by end milling. 3. Addition of substrate loading correction factor using concentration analysis of substrate grindings after magnetic separation of washcoat. 4. Catalyst Analysis Template updated. 5. Minor edits throughout.